

**Patent claims**

1. A process for preparing metal salt nanoparticles (10) in a liquid phase reaction, in which the nanoparticles are synthesized in a synthesis mixture and grow during a synthesis period, characterized by the step of adding a modifying reagent (11) to the synthesis mixture within the synthesis period, with the modifying reagent exhibiting a functional property which is suitable for a subsequent use of the nanoparticles after the synthesis has been concluded.
2. The process as claimed in claim 1, wherein the metal salt nanoparticles are substances which are selected from the series comprising the halides, the alkaline earth metal sulfates, the phosphates and halophosphates, the borates, the vanadates, the aluminates, the silicates, the tungstates, the molybdates and the germanates, all of which can also, in addition, be doped with one or more elements of the lanthanides and/or Mn, Ag, Cu, Pb, Bi, Cr, Sn or Sb.
3. The process as claimed in claim 1, wherein the metal salt nanoparticles are substances selected from the series
  - a)  $XY_2$  ( $X = \text{Mg, Ca, Sr, Ba}$ ;  $Y = \text{F, Cl, I}$ ),  $\text{CaF}_2\text{:Eu(II)}$ ,  $\text{BaF}_2\text{:Eu}$ ;  $\text{BaMgF}_4\text{:Eu}$ ;  $\text{LiBaF}_3\text{:Eu}$ ;  $\text{SrF}_2\text{:Eu}$ ;  $\text{SrBaF}_2\text{:Eu}$ ;  $\text{CaBr}_2\text{:Eu-SiO}_2$ ;  $\text{CaCl}_2\text{:Eu}$ ;  $\text{CaCl}_2\text{:Eu-SiO}_2$ ;  $\text{CaCl}_2\text{:Eu,Mn-SiO}_2$ ;  $\text{CaI}_2\text{:Eu}$ ;  $\text{CaI}_2\text{:Eu,Mn}$ ;  $\text{KMgF}_3\text{:Eu}$ ;  $\text{SrF}_2\text{:Eu(II)}$ ,  $\text{BaF}_2\text{:Eu(II)}$ ,  $\text{YF}_3$ ,  $\text{NaYF}_4$ ,
  - b)  $\text{XSO}_4$  ( $X = \text{Mg, Ca, Sr, Ba}$ ),  $\text{SrSO}_4\text{:Eu}$ ,  $\text{SrSO}_4\text{:Eu,Mn}$ ,  $\text{BaSO}_4\text{:Eu}$ ,  $\text{BaSO}_4\text{:Eu,Mn}$ ,  $\text{CaSO}_4$ ,  $\text{CaSO}_4\text{:Eu}$ ,  $\text{CaSO}_4\text{:Eu,Mn}$ , and also in each case mixed alkaline earth metal sulfates, including those in combination with magnesium, e.g.  $\text{Ca,MgSO}_4\text{:Eu,Mn}$ ,
  - c)  $\text{CaPO}_4\text{:Ce,Mn}$ ,  $\text{Ca}_5(\text{PO}_4)_3\text{Cl:Ce,Mn}$ ,  $\text{Ca}_5(\text{PO}_4)_3\text{F:Ce,Mn}$ ,  $\text{SrPO}_4\text{:Ce,Mn}$ ,  $\text{Sr}_5(\text{PO}_4)_3\text{Cl:Ce,Mn}$ ,  $\text{Sr}_5(\text{PO}_4)_3\text{F:Ce,Mn}$ , this also codoped with  $\text{Eu(II)}$  and  $\text{Eu,Mn}$ ,  $\alpha\text{-Ca}_3(\text{PO}_4)_2\text{:Eu}$ ;

- $\beta$ -Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>:Eu,Mn; Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>Cl:Eu; Sr<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>Cl:Eu;  
 Ba<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>Cl:Eu; Ba<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>Cl:Eu,Mn, Ca<sub>2</sub>Ba<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>Cl:Eu;  
 Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>F:Eu<sup>2+</sup>X<sup>3+</sup>; Sr<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>F:Eu<sup>2+</sup>X<sup>3+</sup> (X=Nd, Er, Ho, Tb);  
 Ba<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>Cl:Eu;  $\beta$ -Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>:Eu; CaB<sub>2</sub>P<sub>2</sub>O<sub>9</sub>:Eu; CaB<sub>2</sub>P<sub>2</sub>O<sub>9</sub>:Eu;  
 Ca<sub>2</sub>P<sub>2</sub>O<sub>7</sub>:Eu; Ca<sub>2</sub>P<sub>2</sub>O<sub>7</sub>:Eu,Mn; Sr<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>Cl<sub>2</sub>:Eu; (Sr, Ca, Ba,  
 Mg)<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>Cl<sub>2</sub>:Eu; LaPO<sub>4</sub>:Ce; CePO<sub>4</sub>,  
 5
- d) LaBO<sub>3</sub>; LaBO<sub>3</sub>:Ce; ScBO<sub>3</sub>:Ce YAlBO<sub>3</sub>:Ce; YBO<sub>3</sub>:Ce; Ca<sub>2</sub>B<sub>5</sub>O<sub>9</sub>Cl:Eu;  
 xEuOyNa<sub>2</sub>OzB<sub>2</sub>O<sub>3</sub>  
 10
- e) YVO<sub>4</sub>, YVO<sub>4</sub>:Eu, YVO<sub>4</sub>:Dy, YVO<sub>4</sub>:Sm, YVO<sub>4</sub>:Bi; YVO<sub>4</sub>:Bi,Eu,  
 YVO<sub>4</sub>:Bi,Dy, YVO<sub>4</sub>:Bi,Sm, YVO<sub>4</sub>:Tm, YVO<sub>4</sub>:Bi,Tm, GdVO<sub>4</sub>,  
 GdVO<sub>4</sub>:Eu, GdVO<sub>4</sub>:Dy, GdVO<sub>4</sub>:Sm, GdVO<sub>4</sub>:Bi; GdVO<sub>4</sub>:Bi,Eu,  
 GdVO<sub>4</sub>:Bi,Dy, GdVO<sub>4</sub>:Bi,Sm.  
 15
- f) MgAl<sub>2</sub>O<sub>4</sub>:Eu; CaAl<sub>2</sub>O<sub>4</sub>:Eu; SrAl<sub>2</sub>O<sub>4</sub>:Eu; BaAl<sub>2</sub>O<sub>4</sub>:Eu;  
 LaMgAl<sub>11</sub>O<sub>19</sub>:Eu; BaMgAl<sub>10</sub>O<sub>17</sub>:Eu; BaMgAl<sub>10</sub>O<sub>17</sub>:Eu, Mn;  
 CaAl<sub>12</sub>O<sub>19</sub>:Eu; SrAl<sub>12</sub>O<sub>19</sub>:Eu; SrMgAl<sub>10</sub>O<sub>17</sub>:Eu; Ba(Al<sub>2</sub>O<sub>3</sub>)<sub>6</sub>:Eu;  
 (Ba,Sr)MgAl<sub>10</sub>O<sub>17</sub>:Eu, Mn; CaAl<sub>2</sub>O<sub>4</sub>:Eu,Nd; SrAl<sub>2</sub>O<sub>4</sub>:Eu, Dy;  
 Sr<sub>4</sub>Al<sub>14</sub>O<sub>25</sub>:Eu,Dy,  
 20
- g) BaSrMgSi<sub>2</sub>O<sub>7</sub>:Eu; Ba<sub>2</sub>MgSiO<sub>7</sub>:Eu; BaMg<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>:Eu; CaMgSi<sub>2</sub>O<sub>6</sub>:Eu;  
 SrBaSiO<sub>4</sub>:Eu; Sr<sub>2</sub>Si<sub>3</sub>O<sub>8</sub>.SrCl<sub>2</sub>:Eu; Ba<sub>5</sub>SiO<sub>4</sub>Br<sub>6</sub>:Eu; Ba<sub>5</sub>SiO<sub>4</sub>Cl<sub>6</sub>:Eu;  
 Ca<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub>:Eu; CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>:Eu; Ca<sub>1.5</sub>Sr<sub>0.5</sub>MgSi<sub>2</sub>O<sub>7</sub>:Eu;  
 (Ca,Sr)<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub>:Eu, Sr<sub>2</sub>LiSiO<sub>4</sub>F:Eu,  
 25
- h) X<sub>3</sub>WO<sub>6</sub> (X = Mg, Ca, Sr, Ba), X<sub>2</sub>WO<sub>4</sub> (X = Li, Na, K, Rb, Cs),  
 XMoO<sub>4</sub> (X = Mg, Ca, Sr, Ba) and also polymolybdates or  
 polytungstates and/or the salts of the corresponding hetero- or isopoly  
 acids  
 30
- i) Zn<sub>2</sub>GeO<sub>4</sub>

j) the following compounds:  $ALnO_2:Yb, Er$  ( $A = Li, Na; Ln = Gd, Y, Lu$ );  $Ln_2O_3:Yb, Er$  ( $Ln = La, Gd, Y, Lu$ );  $LnAO_4:Yb, Er$  ( $Ln = La, Y; A = P, V, As, Nb$ );  $Ca_3Al_2Ge_3O_{12}:Er$ ;  $Gd_2O_2S:Yb, Er$ ;  $La_2S:Yb, Er$ .

5 all of which can also, in addition, be doped with one or more elements of the lanthanides and/or Mn, Ag, Cu, Pb, Bi, Cr, Sn or Sb.

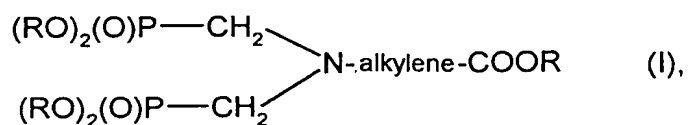
4. The process as claimed in claim 2 or 3, wherein the concentration of the doping elements in the host lattice is between  $10^{-5}$  mol% and 50 mol%,  
10 preferably between 0.01 mol% and 30 mol%, particularly preferably between 0.1 mol% and 20 mol%.

5. The process as claimed in claims 1 to 4, wherein the subsequent use comprises the dispersion of the modified nanoparticles in a solvent which is  
15 specially selected with a view to the application.

6. The process as claimed in one of claims 1 to 5, wherein the modifying reagent also exhibits a growth-controlling function in order to selectively control both the growth of the nanoparticles and the functionality of the  
20 surface, by means of binding to the nanoparticle surface.

7. The process as claimed in one of claims 1 to 5, wherein use is made, as modifying reagent (11), of a pentaalkyl iminobis(methylenephosphono)-carboxylate of the formula I:

25



where

30 R is a  $C_1$ - $C_4$ -alkyl radical, and

alkylene is a C<sub>1</sub>-C<sub>22</sub>-alkylene radical or C<sub>7</sub>-C<sub>20</sub>-alkylenearylene radical, preferably a C<sub>5</sub>-C<sub>17</sub>-alkylene radical, which can be linear or branched and can, in addition, carry, as additional substituents, halogen atoms, COOR groups, alkoxy groups, bis(dialkoxyphosphorylmethyl)amino groups or aryl radicals.

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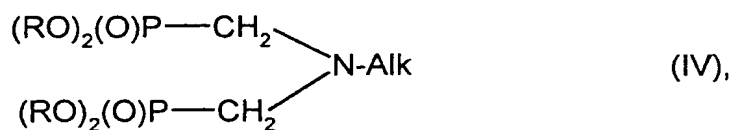
8. The process as claimed in one of claims 1 to 5, wherein use is made, as modifying reagent (11), of a pentaethyl or a pentaisopropyl iminobis-(methylenephosphono)undecanoate.

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9. The process as claimed in one of claims 1 to 5, wherein use is made, as modifying reagent (11), of a pentaethyl or pentaisopropyl iminobis-(methylenephosphono)caproate.

10. The process as claimed in the preceding claims 1 to 9, wherein the time which elapses during the synthesis period before the modifying reagent (11) is added is directly proportional to the planned average size of the nanoparticles.

11. The use of compounds of the formula IV as modifying reagent (11) for preparing metal salt nanoparticles in accordance with the process as claimed in claims 1 to 4:



25

where

R has the meaning given above with regard to formula (I), and

30

Alk is a C<sub>4</sub>-C<sub>22</sub>-alkyl radical or C<sub>7</sub>-C<sub>30</sub> aralkyl or arylalkyl radical.

12. The use of the nanoparticles which are prepared as claimed in one of the preceding claims 1 to 10 for coupling to biologically relevant molecules for the purpose of marking them.
- 5
13. The use of the nanoparticles which are prepared as claimed in one of the preceding claims 1 to 10 for a subsequent intended application which requires the nanoparticles to be coupled to application-specific molecules, with the coupling being selectively promoted or made possible by means of one of the functional properties of the modifying reagent (11).
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